

Adhesion of Water on Flat Polymer Surfaces and Superhydrophobic Surfaces

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ABSTRACT

The interactions between water and surfaces of varying hydrophobicity have been studied using a high-sensitivity microelectromechanical balance system (tensiometer). The surfaces studied include solution coated polymer films, commercial plastic sheets, self-assembled polymer layers on Si-wafer, fluorinated textured surfaces on Si-wafer, CVD polymerized films, and rose petals. Static contact angle data indicate that these surfaces varying from hydrophilic to superhydrophobic, from smooth and flat to rough and textured. While the wetting force of water on these surfaces was found to correlate well to the advancing water contact angle, the same could not be said about the pull off force, which is a measure of adhesion between the water droplet and the surface of interest. Rather the pull off force was shown to correlate well to the receding contact angle. Evidence is provided that the adhesion between water and the rough surface can be as strong as the flat polymer surface when the water droplet is in the Wenzel state on the rough surface. Finally, adhesion of water was found to play a role to the quality of the detachment of the water droplet from a surface. A minute amount of water residue could be found on certain surfaces after pull-off. The correlation between the quality of detachment and the receding contact angle is discussed.

Keywords: wetting, adhesion, contact angle, sliding angle, superhydrophobicity, polymer surfaces, rose petals

1 INTRODUCTION

The interplay between the adhesion of imaging materials (ink and toner) on various print surfaces versus the cohesive forces within the patches or droplets of these imaging materials play a crucial role in print hardware design and print process development [1,2]. If the imaging material adheres strongly on the print surface, particularly when the work-of-adhesion is stronger than the cohesive force, patches or droplets of image materials may break and a small amount of imaging materials may leave behind the print surface after contact. This will result in image quality defect, an undesirable effect in printing [3]. In this work, we attempted to measure the attractive and adhesive interactions of organic liquids, such as hexadecane and molten solid ink, on a microelectromechanical balance system (tensiometer) and then correlate them with surface property data. Our

initial scoping experiments were not successful due to difficulties in handling low surface tension liquids. For the sake of experimental procedure development and to find out if there are correlations between attractive/adhesive forces and the surface properties, we use water in our model investigation. The surface tension of water is at 72.5 mN/m and is three times higher than those of hexadecane and solid ink. Here we report the static and dynamic (advancing, receding and sliding) contact angle measurements of water on 20 different surfaces. The correlation between the force data from the tensiometer and the surface property data are presented and discussed.

2 EXPERIMENTAL

The surfaces studied in this work include solution coated polymer films (Table 1, 1 - 3, 6 and 13), commercial plastic sheets (4, 5, 14), self-assembled polymer layers on Si-wafer (10, 11), CVD polymerized films (7 - 9, 12) [4], fluorinated textured surfaces on Si-wafer (Table 2, 15 - 18), [5] and rose petals (19, 20). Contact angle and sliding angle measurements were performed on a goniometer model OCA20 from Dataphysics using DI water as the test liquid. The size of the drop was controlled to be $\sim 5 \mu\text{L}$. For dynamic measurements, advancing angle was measured by adding a small volume of water to the surface; and the receding angle was measured by slowly removing water from the drop ($0.15 \mu\text{L/s}$). Sliding angle measurement was done by tilting the base unit at a rate of $1^\circ/\text{sec}$ with a $\sim 10 \mu\text{L}$ droplet using titling base unit TBU90E. The sliding angle is defined as the angle where the test liquid droplet starts to slide (or move).

The interaction of water with different surfaces was studied on a high-sensitivity microelectromechanical balance system or a tensiometer (Dataphysics DCAT 21, Germany). A hydrophilic platinum/iridium ring suspended with a 5 mg deionized water droplet was connected to the cantilever, and the force of this balance system was initialized to zero initially. The substrate was then placed on the sample table which was raised up at a speed of 0.03 mm/s toward the water droplet and the surface was considered "touched" when the force change was larger than 0.3 mg (or $2.9 \mu\text{N}$). At the point of contact, the snap-in force was recorded. The substrate surface continued to move up for another 0.1 mm. After that, the surface and the water droplet retracted or separated at a speed of 0.01 mm/s. At the point of separation, the pull-off force was

recorded. The entire procedure was performed in lab ambient. The relation between the interactive forces (both attraction and separation) and the distance (or time) were recorded automatically and analyzed by the software.

3 RESULTS AND DISCUSSION

3.1 Contact Angle Measurement of Water on Different Surfaces

Flat Surfaces. The surfaces of 14 different polymer surfaces obtained from different sources were studied by both static and dynamic contact angle measurement techniques. Table 1 summarizes the surfaces/materials studied and their static contact angle, sliding angle, advancing contact angle and receding contact angle. The results show that these surfaces vary from hydrophilic for **1** to highly hydrophobic for **14**. It is also important to note that, some surfaces are very smooth (on Si wafer) and others may have a different degree of roughness due to their coating or fabrication process. Thus surfaces **1** – **14** represent a snap shot of surfaces of all traits.

Table 1. Water contact angle data on flat polymer surfaces.

	Surfaces	θ^a	θ_A^b	θ_R^c	α^d
1	Polyurethane (PU)	70.5°	85°	48.9°	51°
2	PU – 2% Silclean	98.2°	104.3°	76.3°	31°
3	PU – 8% Silclean	104.3°	105.9°	88.1°	23°
4	Polyimide	80.1°	82.5°	56.1°	26.4°
5	Plexiglass	86.5°	93.9°	77.3°	29.1°
6	Polycarbonate	92.4°	98.2°	68.1°	59.2°
7	i-CVD Silicone	87.9°	91.2°	62.2°	90° ^e
8	i-CVD Fluorosilicone	115.9°	118°	90.3°	18.2°
9	i-CVD PTFE	127.7°	134.9°	73.6°	90° ^e
10	SAM OTS	109°	117.4°	94.6°	13°
11	SAM FOTS	107.3°	116°	95°	13.6°
12	Perfluoroacrylate polymer	113°	113.1°	61°	90° ^e
13	Hydrophobic sol gel coating	112.2°	111.6°	92.4°	5.6°
14	PTFE	117.7°	126.6°	91.9°	64.3°

(a) static contact angle; (b) advancing contact angle, (c) receding contact angle, (d) sliding angle; estimated errors are all < 3°, and (e) upper limit of the tilting unit, water drop does not slide even at 90°.

Rough/Textured Surfaces. In an attempt to generalize the conclusion in this work, we extend our study to superhydrophobic textured surfaces and two natural rough surfaces in the front and back side of the rose petals. The superhydrophobic textured surfaces was made using photolithography, followed by surface modification with a fluorosilane and the preparative procedure has been outlined elsewhere [5]. The rose petals were home grown flower picked from Law’s garden in Penfield, New York. The contact angle measurement data for these surfaces are summarized in Table 2. The results indicate that water droplets are in the Cassie Baxter state on surfaces **15** – **19**,

whereas the water drop is in the Wenzel state on surface **20**, the back side of the rose petal [6].

Table 2. Water contact angle data on rough surfaces.

No	Si textured surface (pillar diameter/spacing)	θ^a	θ_A^b	θ_R^c	α^d
15	3 μm /4.5 μm	149°	160°	130.8°	20°
16	3 μm /6 μm	156.2°	161.3°	142.6°	10.1°
17	3 μm /9 μm	154.1°	159.9°	148.9°	5.7°
18	3 μm /12 μm	156.2°	160.8°	151.8°	3.4°
19	Rose petal - front	144.7°	150.7°	131.6°	6.1°
20	Rose petal - back	132.4°	136.6°	85.7°	90° ^e

a - e, same as Table 1.

3.2 Adhesion Measurements of Water on Different Surfaces

The interactive forces between water and various surfaces were studied on a tensiometer. Figures 1a-1d depict a series of photographs showing the inside view of the chamber of the tensiometer.

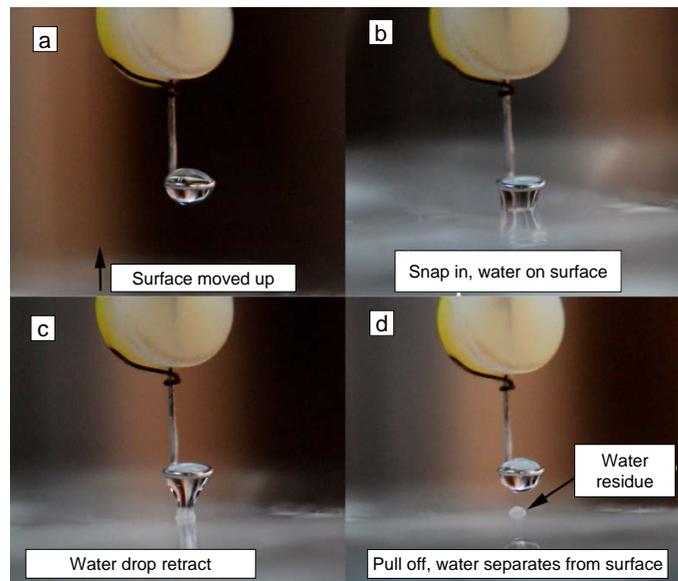


Figure 1 Photographs inside the sample chamber of the microelectromechanical balance system: (a) measuring surface moves upward towards the water droplet, (b) surface makes contact to the water droplet, (c) surface starts to retract separating from the water droplet, and (d) surface separates from the water droplet leaving a small drop of water residue on the surface.

The figure also stepwise illustrates how the experiment was performed. Firstly, 5 mg of deionized water was placed on the platinum/iridium ring, which was connected to the cantilever. The force of this balance system was initialized to zero and the surface of the substrate was moved upwards at a speed of 0.03 mm/s as shown in Figure 1a. As the surface and the water droplet approached and “touched”,

the attractive, wetting force was detected and measured as the snap-in force (Figure 1b). After the snap-in, the surface continued to move ~ 0.1 mm closer to the ring probe. At this point, the surface was retracted (at a speed of 0.01 mm/s) from the water droplet and the maximum force was recorded (Figure 1c). Depending on the nature of the surface, a very small drop of water residue might leave behind after the water droplet is pulled off from the surface (Figure 1d). At the point of separation, the pull-off force was recorded. The relation between the interactive forces and the distance (or time) was recorded automatically by the tensiometer. A typical output for the entire experiment is given in Figure 2.

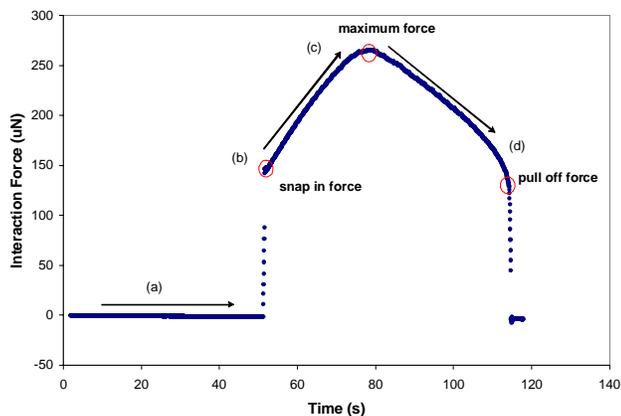


Fig. 2 A typical experiment output from the tensiometer

Among the data points in Figure 2, the snap-in force and pull-off force are most relevant to this work. The former measures the wetting force when the water droplet first interacts with the surface. The pull-off force is a little bit more complicated. The force recorded at pull-off will depend on how or when the water droplet is separated from the surface. When the separation is clean where no water residue is observed after the separation, the pull-off force is the adhesion force between the water drop and the surface at vertical separation. On the other hand, when water residue is observed on the surface after pull-off, it implies that the adhesion between the surface and the water droplet is stronger than the cohesive force within the water droplet. What's recorded then is the force when the water droplet breaks. The magnitude of this force is related to the work-of-adhesion between water and the surface, cohesive force of the water droplet (surface tension) and the contact area when the water droplet breaks. Detailed analysis of this force is beyond the scope of this investigation. In this work, our main concern is the snap-in force and the pull-off force for surfaces 1 – 20.

3.3 Correlation of Water Adhesion to Contact Angle Data

Figure 3 depicts the plot of the snap-in force as a function of the advancing contact angle and a fairly good correlation is obtained. The snap-in, wetting force is shown to decrease

as the advancing contact angle increases and becomes negligible when the surface is superhydrophobic. The result makes sense because the motion of “snapping in” is very similar to the advancing of the contact line during the advancing contact measurement.

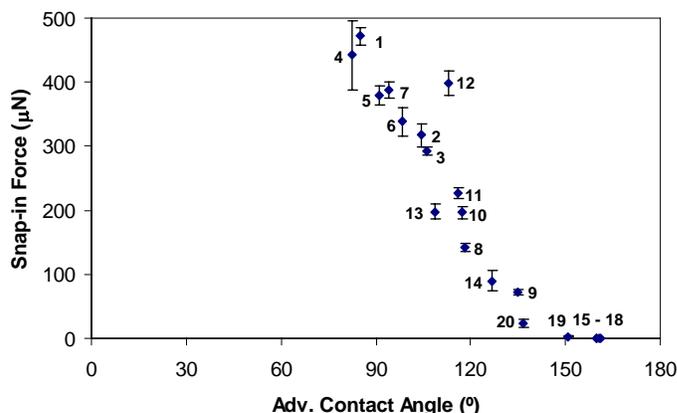


Fig. 3 Plot of snap-in force measured on tensiometer versus advancing contact angle.

Numerous attempts were made, but fail to correlate the pull-off force with contact angle parameters that are known to relate to adhesion, such as sliding angle, contact angle hysteresis and $(\cos\theta_R - \cos\theta_A)$. On the other hand, a good correlation is obtained when we plot the pull-off force versus the receding contact angle (Figure 4). The pull-off, adhesion force between water and the surface is shown to decrease monotonously as the receding contact angle increases.

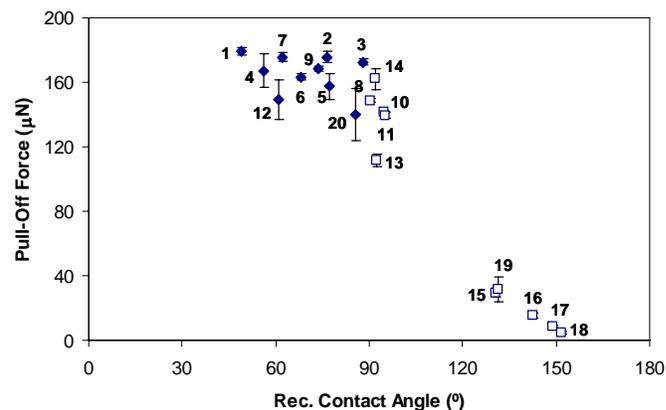


Fig. 4 Plot of the pull-off force for all surfaces measured on the tensiometer versus receding contact angle.

Another silent feature of the data in Figure 4 lies in the labeling. As noted earlier, water drop may break off differently during the pull-off: □ denotes to a clean break where no water residue was observed and ● indicates the presence of water residue after pull-off. A glance of the plot in Figure 4 reveals a remarkable trend. For surfaces with receding angle $> \sim 90^\circ$, the water-surface separation is

clean, whereas residual water drops are observed for surfaces with receding angle $< \sim 90^\circ$. While this may be intuitively expected because surfaces with low receding contact angle should have high adhesion. What's amazing is the clean transition from bad separation to good separation.

4 CONCLUDING REMARKS

This work shows with great generality that the wetting force correlates well to the advancing contact angle and the adhesion force correlates to the receding contact angle, the lower the receding angle the stronger the adhesion force towards the liquid. In case of water, this work also demonstrates that when the receding angle is $< 90^\circ$, the adhesion force becomes stronger than the cohesion of the water droplet. This results in breakage of the water droplet during pull-off. As noted in the introductory section, water was used as a model liquid to study the tool to investigate the intricate relationship between surface property and adhesion; our next attention will be focused on applying the tool and the understanding to study low tension liquids.

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